

1. A method of inhibiting the corrosion of metal surfaces contacted by an aqueous acid solution comprising:

(a) combining a corrosion inhibiting composition with said aqueous acid solution, said corrosion inhibiting composition comprising the reaction product of an alpha,beta-unsaturated aldehyde or ketone with a primary or secondary amine; and then

(b) contacting said metal surfaces with said aqueous acid solution containing said reaction product.

2. The method claim 1 wherein said alpha,beta-unsaturated aldehyde or ketone and said primary or secondary amine are separately added to water used to form said aqueous acid solution wherein said alpha,beta-unsaturated aldehyde or ketone and said primary or secondary amine react and form said corrosion inhibiting reaction product therein.

3. The method of claim 1 wherein said metal surfaces comprise metals selected from the group consisting of J55 steel, N-80 steel, 13Cr alloy, 25 Cr alloy, Incoloy 825 and 316L.

4. The method of claim 1 wherein said alpha,beta-unsaturated aldehyde is selected from the group consisting of: crotonaldehyde, 2-hexenal; 2-heptenal, 2-octenal; 2-nonenal, 2-decenal, 2-undecenal, 2-dodecenal, 2,4-hexadienal, 2,4-heptadienal, 2,4-octadienal, 2,4-nonadienal, 2,4-decadienal, 2,4-undecadienal, 2,4-dodecadienal, 2,6-dodecadienal, citral; 1-formyl-[2-(2-methylvinyl)]-2-n-octylethylene, cinnamaldehyde, dicinnamaldehyde, p-hydroxycinnamaldehyde, p-methylcinnamaldehyde, p-ethylcinnamaldehyde, p-methoxycinnamaldehyde, p-dimethylaminocinnamaldehyde, p-diethylaminocinnamaldehyde, p-

methoxycinnamaldehyde, p-dimethylaminocinnamaldehyde, p-diethylaminocinnamaldehyde, p-nitrocinnamaldehyde, o-nitrocinnamaldehyde, o-allyloxycinnamaldehyde, 4-(3-propenal)cinnamaldehyde, p-sodium sulfocinnamaldehyde, p-trimethylammoniumcinnamaldehyde sulfate, p-trimethylammoniumcinnamaldehyde o-methylsulfate, p-thiocyanocinnamaldehyde, p-(S-acetyl)thiocinnamaldehyde, p-(S-N,N-dimethylcarbamoylethio)cinnamaldehyde, p-chlorocinnamaldehyde, 5-phenyl-2,4-pentadienal, 7-phenyl-2,4,6-heptatrienal, 5-(p-methoxyphenyl)-2,4-pentadienal; 2,3-diphenylacrolein, 3,3-diphenylacrolein,  $\alpha$ -methylcinnamaldehyde,  $\beta$ -methylcinnamaldehyde,  $\alpha$ -chlorocinnamaldehyde,  $\alpha$ -bromocinnamaldehyde,  $\alpha$ -butylcinnamaldehyde,  $\alpha$ -amylcinnamaldehyde,  $\alpha$ -hexylcinnamaldehyde; 2-(p-methylbenzylidene)decanal,  $\alpha$ -bromo-p-cyanocinnamaldehyde,  $\alpha$ -ethyl-p-methylcinnamaldehyde, p-methyl- $\alpha$ -pentylcinnamaldehyde, 3,4-dimethoxy- $\alpha$ -methylcinnamaldehyde,  $\alpha$ -[(4-methylphenyl)methylene]benzeneacetaldehyde,  $\alpha$ -(hydroxymethylene)-4-methylbenzylacetaldehyde, 4-chloro- $\alpha$ -(hydroxymethylene)benzeneacetaldehyde,  $\alpha$ -nonylidenebenzeneacetaldehyde, 3,7-dimethyl-2,6-octadienal, and beta-hydroxy aldehydes which dehydrate to form alpha,beta-unsaturated aldehydes under acidic conditions; and said alpha,beta-unsaturated ketones are selected from the group consisting of: 4-phenyl-3-buten-2-one, 3-methyl-1-phenyl-2-buten-1-one; 4-phenyl-3-penten-2-one; 5-phenyl-4-penten-3-one; 6-phenyl-5-hexen-4-one; 7-phenyl-6-hepten-4-one-2-ol; 7-phenyl-6-hepten-4-one; 1,3-diphenyl-2-propen-1-one; 1,3-diphenyl-2-buten-1-one; dicinnamalacetone; 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione mesityl oxide; phorone; isophorone; 3-methyl-2-cyclohexen-1-one; 3,6-dimethyl-2,6-cycloheptadien-1-one; 5-methyl-4-hexen-3-one; and beta-hydroxy ketones which dehydrate to form alpha,beta-unsaturated ketones under acidic conditions.

5. The method of claim 1 wherein said primary or secondary amine is selected from the group consisting of ethanolamine, diethanolamine, partially ethoxylated dehydroabietylamine, ethylamine, diethylamine, dehydroabietylamine, propylamine, dipropylamine, propanolamine, isopropanolamine, 2-propanol-1-amine, diisopropanolamine, butylamine, dibutylamine, tert-butylamine, pentylamine, dipentylamine and tert-benzyl-tert-butylamine.

6. The method of claim 1 wherein said reaction product results from the reaction of said primary or secondary amine with said alpha,beta-unsaturated aldehyde or ketone at a molar ratio of amine to aldehyde or ketone in the range of from about 0.1:1 to about 4:1.

7. The method of claim 1 wherein said corrosion inhibiting composition is combined with said aqueous acid solution in an amount in the range of from about 0.01% to about 5% by weight of said aqueous acid fluid.

8. The method of claim 1 wherein said corrosion inhibiting composition further comprises one or more of an iodide source, a solvent or a surfactant.

9. The method of claim 1 wherein said aqueous solution comprises water and an acid selected from the group consisting of hydrochloric acid, acetic acid, formic acid, hydrofluoric acid and mixtures thereof.

10. The method of claim 1 wherein said aqueous acid solution comprises water and hydrochloric acid, said hydrochloric acid being present in an amount in the range of from about 5% to about 28% by weight of aqueous acid fluid.

11. The method of claim 1 which further comprises contacting said metal surfaces with said aqueous acid solution at temperatures up to about 300°F when said aqueous acid solution comprises hydrochloric acid at a concentration of about 15% by weight thereof.

12. The method of claim 1 which further comprises contacting said metal surfaces with said aqueous acid fluid at temperatures up to about 225°F when said aqueous acid solution comprises hydrochloric acid at a concentration of about 28% by weight thereof.

13. A corrosion inhibiting composition for inhibiting the corrosion of metal surfaces by an aqueous acid solution when the composition is added to the aqueous acid solution comprising the reaction product of an alpha,beta-unsaturated aldehyde or ketone with a primary or secondary amine.

14. The corrosion inhibiting composition of claim 13 wherein said alpha,beta-unsaturated aldehyde is selected from the group consisting of: crotonaldehyde, 2-hexenal; 2-heptenal, 2-octenal; 2-nonenal, 2-decenal, 2-undecenal, 2-dodecenal, 2,4-hexadienal, 2,4-heptadienal, 2,4-octadienal, 2,4-nonadienal, 2,4-decadienal, 2,4-undecadienal, 2,4-dodecadienal, 2,6-dodecadienal, citral; 1-formyl-[2-(2-methylvinyl)]-2-n-octylethylene, cinnamaldehyde, dicinnamaldehyde, p-hydroxycinnamaldehyde, p-methylcinnamaldehyde, p-ethylcinnamaldehyde, p-methoxycinnamaldehyde, p-dimethylaminocinnamaldehyde, p-diethylaminocinnamaldehyde, p-nitrocinnamaldehyde, o-nitrocinnamaldehyde, o-allyloxycinnamaldehyde, 4-(3-propenal)cinnamaldehyde, p-sodium sulfocinnamaldehyde, p-trimethylammoniumcinnamaldehyde sulfate, p-trimethylammoniumcinnamaldehyde o-methylsulfate, p-thiocyanocinnamaldehyde, p-(S-acetyl)thiocinnamaldehyde, p-(S-N,N-dimethylcarbamoylthio)cinnamaldehyde, p-chlorocinnamaldehyde, 5-phenyl-2,4-pentadienal, 7-phenyl-2,4,6-heptatrienal, 5-(p-methoxyphenyl)-2,4-pentadienal; 2,3-diphenylacrolein, 3,3-

diphenylacrolein,  $\alpha$ -methylcinnamaldehyde,  $\beta$ -methylcinnamaldehyde,  $\alpha$ -chlorocinnamaldehyde,  $\alpha$ -bromocinnamaldehyde,  $\alpha$ -butylcinnamaldehyde,  $\alpha$ -amylcinnamaldehyde,  $\alpha$ -hexylcinnamaldehyde; 2-(p-methylbenzylidene)decanal,  $\alpha$ -bromo-p-cyanocinnamaldehyde,  $\alpha$ -ethyl-p-methylcinnamaldehyde, p-methyl- $\alpha$ -pentylcinnamaldehyde, 3,4-dimethoxy- $\alpha$ -methylcinnamaldehyde,  $\alpha$ -[(4-methylphenyl)methylene]benzeneacetaldehyde,  $\alpha$ -(hydroxymethylene)-4-methylbenzylacetaldehyde, 4-chloro- $\alpha$ -(hydroxymethylene)benzeneacetaldehyde,  $\alpha$ -nonylidenebenzeneacetaldehyde, and 3,7-dimethyl-2,6-octadienal and beta-hydroxy aldehydes which dehydrate to form alpha,beta-unsaturated aldehydes under acidic conditions; said alpha,beta-unsaturated ketone is selected from the group consisting of: 4-phenyl-3-buten-2-one, 3-methyl-1-phenyl-2-buten-1-one; 4-phenyl-3-penten-2-one; 5-phenyl-4-penten-3-one; 6-phenyl-5-hexen-4-one; 7-phenyl-6-hepten-4-one-2-ol; 7-phenyl-6-hepten-4-one; 1,3-diphenyl-2-propen-1-one; 1,3-dephenyl-2-buten-1-one; dicinnamalacetone; 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, mesityl oxide; phorone; isophorone; 3-methyl-2-cyclohexen-1-one; 3,6-dimethyl-2,6-cycloheptadien-1-one; 5-methyl-4-hexen-3-one; and beta-hydroxy aldehydes or ketones which dehydrate to form the alpha,beta-unsaturated aldehydes or ketones under acidic conditions.

15. The corrosion inhibiting composition of claim 13 wherein said primary or secondary amines are selected from the group consisting of ethanolamine, diethanolamine, partially ethoxylated dehydrobietylamine, ethylamine, diethylamine, dehydroabietylamine, propylamine, dipropylamine, propanolamine, isopropanolamine, 2-propanol-1-amine, diisopropanolamine, butylamine, dibutylamine, tert-butylamine, pentylamine, dipentylamine and tert-benzyl-tert-butylamine.

16. The corrosion inhibiting composition of claim 13 wherein said reaction product results from the reaction of said alpha,beta-unsaturated aldehyde or ketone with said primary or secondary amine at a molar ratio of amine to aldehyde or ketone in the range of from about 0.1:1 to about 4:1.

17. The corrosion inhibiting composition of claim 13 which further comprises one or more of an iodide source, a solvent or a surfactant.

18. A metal corrosion inhibited aqueous acid composition comprising:  
water;  
an acid selected from the group consisting of hydrochloric acid, acetic acid, formic acid, hydrofluoric acid and mixtures thereof; and  
a corrosion inhibiting composition comprising the reaction product of an alpha,beta-unsaturated aldehyde or ketone with a primary or secondary amine.

19. The aqueous acid composition of claim 18 wherein said acid is hydrochloric acid and is present in said composition in an amount in the range of from about 5% to about 28% by weight of said water.

20. The aqueous acid composition of claim 18 wherein said alpha,beta-unsaturated aldehyde is selected from the group consisting of: crotonaldehyde, 2-hexenal; 2-heptenal, 2-octenal; 2-nonenal, 2-decenal, 2-undecenal, 2-dodecenal, 2,4-hexadienal, 2,4-heptadienal, 2,4-octadienal, 2,4-nonadienal, 2,4-decadienal, 2,4-undecadienal, 2,4-dodecadienal, 2,6-dodecadienal, citral; 1-formyl-[2-(2-methylvinyl)]-2-n-octylethylene, cinnamaldehyde, dicinnamaldehyde, p-hydroxycinnamaldehyde, p-methylcinnamaldehyde, p-ethylcinnamaldehyde, p-methoxycinnamaldehyde, p-dimethylaminocinnamaldehyde, p-

diethylaminocinnamaldehyde, p-nitrocinnamaldehyde, o-nitrocinnamaldehyde, o-allyloxycinnamaldehyde, 4-(3-propenal)cinnamaldehyde, p-sodium sulfocinnamaldehyde, p-trimethylammoniumcinnamaldehyde sulfate, p-trimethylammoniumcinnamaldehyde o-methylsulfate, p-thiocyanocinnamaldehyde, p-(S-acetyl)thiocinnamaldehyde, p-(S-N,N-dimethylcarbamoylthio)cinnamaldehyde, p-chlorocinnamaldehyde, 5-phenyl-2,4-pentadienal, 7-phenyl-2,4,6-heptatrienal, 5-(p-methoxyphenyl)-2,4-pentadienal; 2,3-diphenylacrolein, 3,3-diphenylacrolein,  $\alpha$ -methylcinnamaldehyde,  $\beta$ -methylcinnamaldehyde,  $\alpha$ -chlorocinnamaldehyde,  $\alpha$ -bromocinnamaldehyde,  $\alpha$ -butylcinnamaldehyde,  $\alpha$ -amylcinnamaldehyde,  $\alpha$ -hexylcinnamaldehyde; 2-(p-methylbenzylidene)decanal,  $\alpha$ -bromo-p-cyanocinnamaldehyde,  $\alpha$ -ethyl-p-methylcinnamaldehyde, p-methyl- $\alpha$ -pentylcinnamaldehyde, 3,4-dimethoxy- $\alpha$ -methylcinnamaldehyde,  $\alpha$ -[(4-methylphenyl)methylene]benzeneacetaldehyde,  $\alpha$ -(hydroxymethylene)-4-methylbenzylacetaldehyde, 4-chloro- $\alpha$ -(hydroxymethylene)benzeneacetaldehyde,  $\alpha$ -nonylidenebenzeneacetaldehyde, and 3,7-dimethyl-2,6-octadienal and beta-hydroxy aldehydes which dehydrate to form alpha,beta-unsaturated aldehydes under acidic conditions; and said alpha,beta-unsaturated ketone is selected from the group consisting of: 4-phenyl-3-buten-2-one, 3-methyl-1-phenyl-2-buten-1-one; 4-phenyl-3-penten-2-one; 5-phenyl-4-penten-3-one; 6-phenyl-5-hexen-4-one; 7-phenyl-6-hepten-4-one-2-ol; 7-phenyl-6-hepten-4-one; 1,3-diphenyl-2-propen-1-one; 1,3-diphenyl-2-buten-1-one; dicinnamalacetone; 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione mesityl oxide; phorone; isophorone; 3-methyl-2-cyclohexen-1-one; 3,6-dimethyl-2,6-cycloheptadien-1-one; 5-methyl-4-hexen-3-one; and beta-hydroxy ketones which dehydrate to form the alpha,beta-unsaturated ketones under acidic conditions.

21. The aqueous acid composition of claim 18 wherein said primary or secondary amine is selected from the group consisting of ethanolamine, diethanolamine, partially ethoxylated dehydrobiethylamine, ethylamine, diethylamine, dehydroabiethylamine, propylamine, dipropylamine, propanolamine, isopropanolamine, 2-propanol-1-amine, diisopropanolamine, butylamine, dibutylamine, tert-butylamine, pentylamine, dipentylamine and tert-benzyl-tert-butylamine.

22. The aqueous acid composition of claim 18 wherein said reaction product results from reaction of said primary or secondary amine with said alpha,beta-unsaturated aldehyde or ketone at a molar ratio of amine to aldehyde or ketone in the range of from about 0.1:1 to about 4:1.

23. The aqueous acid composition of claim 18 wherein said corrosion inhibiting composition is present in said composition in an amount in the range of from about 0.01% to about 5% by volume of aqueous acid fluid.

24. The aqueous acid composition of claim 18 which further comprises one or more of an iodide source, a solvent or a surfactant.